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Thermal reactions of hexafluoro-1,3-butadiene. Part I. Primary products and their thermal transformations

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Abstract

Depending on the temperature, the thermal reactions of hexafluoro-1,3-butadiene include intra- and/or intermolecular cycloaddition and give hexafluorocyclobutene, [2+4]- and [2+2]-cycloadducts as primary products. The latter react with hexafluorobutadiene to give its trimers while the [2+2]-cycloadduct, being generated as two isomers, undergoes some thermal rearrangements in addition. Thus, *cis*-perfluorodivinylcyclobutane is isomerized at 150 °C to perfluorotricyclo[4.2.0.0^{2,5}]- and -[3.3.0.0^{2,6}]octanes together with unstable, easily polymerized, *cis,trans*-perfluoro-1,5-cyclo-octadiene. The *trans* isomer is isomerized at 200 °C to perfluorovinyl-4-cyclohexene and perfluorotricyclo[3.3.0.0^{2,6}]octane. Possible schemes for the formation of the latter are discussed. Racemic *trans,trans*-perfluoro-1,5-cyclo-octadiene is argued to be a precursor of perfluorotricyclo[3.3.0.0^{2,6}]octane in the isomerizations of both the *cis*- and *trans*-[2+2]-cycloadducts.

Introduction

The thermal reactions of conjugated 1,3-dienes have been studied thoroughly in the case of 1,3-butadiene. The primary products of these reactions are [2+4]- and [2+2]-cyclodimers [1–7]. In contrast to conjugated 1,3-butadiene which acts as a diene donor in cycloaddition reactions, *F*-butadiene** is characterized by acceptor properties and a breach of conjugation because of its molecular non-planarity. This dissimilarity implies differences in the reaction ability of the two dienes and explains our interest in the thermal transformation of *F*-butadiene. These transformations have been studied previously by Prober and Miller [8] who obtained *F*-cyclobutene [9] together with mixtures of *F*-butadiene dimers and trimers of unknown structure. Subsequently, the structure of one of these dimers, i.e. *F*-tricyclo-[3.3.0.0^{2,6}]octane (**1**), was established by X-ray analysis [10].

This and a following report [11] present evidence that the thermal reactions of *F*-butadiene yield dimers **2–6** and trimers **7–11** along with *F*-

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***F*- corresponds to perfluoro-.

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cyclobutene and dimer **1**. A description is also provided of the mutual transformations of the products obtained, part of which is represented in Scheme 1 (the formation and transformations of the trimers are described in ref. 11).

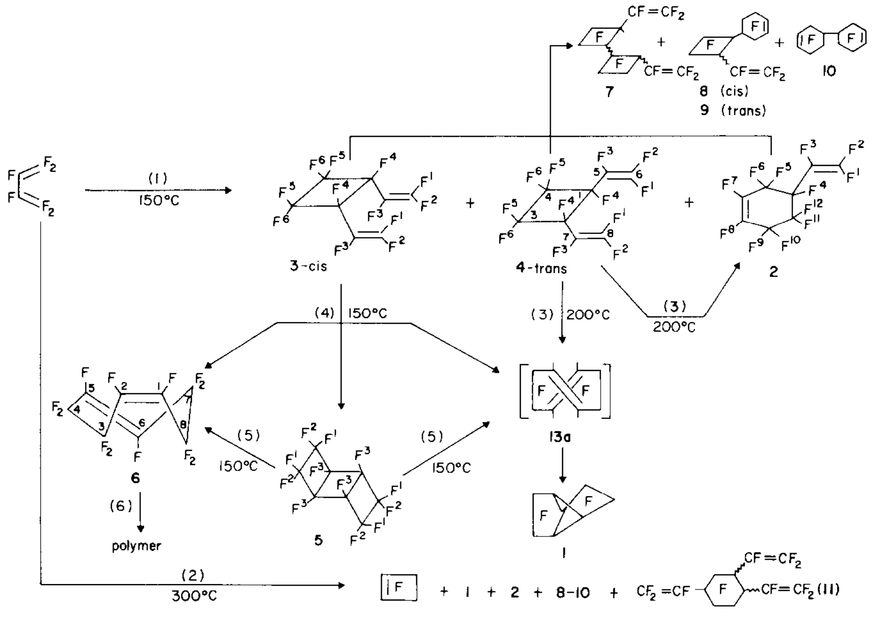
Results and discussion

Primary products

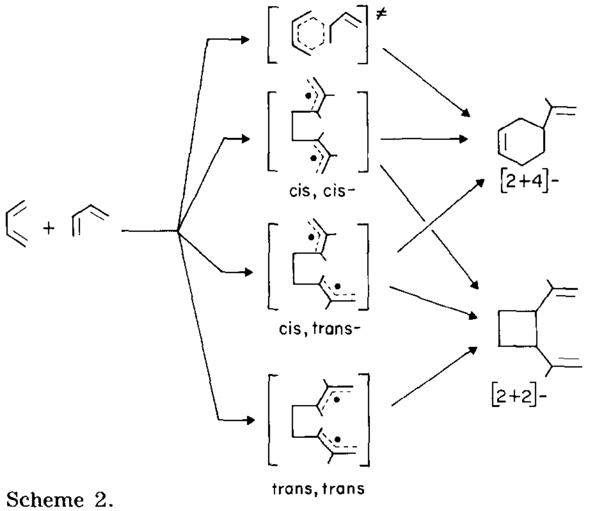
Prolonged heating (150 °C) of *F*-butadiene affords dimers **3–5**, trimers **7–10** and traces of dimer **1** [Scheme 1, reaction (1)]. As will be demonstrated, the primary products of reaction (1) are the [2+4]- and [2+2]-cycloadducts **2–4** (cf. refs. 2 and 3). We were not able to detect the [2+4]-cyclodimer **2** among the products of reaction (1); however, its formation is confirmed by the presence of trimers **8–10** which include the cyclohexene moiety. In fact, under the conditions of reaction (1), the dimers **3** and **4** are not isomerized to dimer **2** (see below) and neither are the trimers **7** isomerized to the trimers **8–10** [11]. It follows, therefore, that only dimer **2**, which is one of the primary products, is responsible for the formation of trimers **8–10**.

Hence, the distinctions between the thermal reactions of butadiene and *F*-butadiene are exhibited only in the ratios of the [2+4]- and [2+2]-cyclodimers formed, probably reflecting the different contributions of these dienes to competing concerted and stepwise cycloadditions (Scheme 2).

The formation of [2+2]-cyclodimers as the main primary products of reaction (1) suggests a participation of biradical intermediates (cf. refs. 5



Scheme 1.



Scheme 2.

and 6). As can be seen from Scheme 2, all the biradicals are capable of being stabilized by cyclization to the [2 + 2]-adducts **3**, **4** whereas the *cis,cis* and *cis,trans* biradicals, in addition, are able to undergo ring closure to form the [2 + 4]-adduct **2**. Although concerted [2 + 4]-cycloaddition is not excluded as a competing reaction, and dimer **2** is much more stable than dimers **3**, **4** (see below), formation of the latter turns out to be preferable (at 150 °C the [2 + 4]/[2 + 2] ratio is *c*. 15:85*, cf. ref. 1), which supports a stepwise mechanism for the thermal reactions of *F*-butadiene.

In addition to the primary products described, reaction (1) also yields the non-trivial *F*-butadiene dimers **1** and **5**, a process requiring special interpretation. Since the formation of dimers of type **5** in thermal reactions of dienes has no analogues and the mechanism for the formation of dimer **1** has yet to be examined, we have proceeded from the assumption that these dimers are secondary products. In order to propose a reasonable mechanism for their formation, we have studied the thermal stability of dimers **2–4** and trimers **7–10** and also undertaken the thermal reaction of *F*-butadiene at 300 °C [Scheme 1, reaction (2)]. An analysis of the composition of the products of reaction (2) shows that the primary products are not only dimers **2–4** [as in reaction (1)], but also *F*-cyclobutene in the form of the cyclic isomer of *F*-butadiene (cf. ref. 9). The absence of the dimers **3** and **4** and of the trimer **7** from the products of reaction (2) [cf. reaction (1)] shows that they are capable of thermal transformation. Dimer **2** and trimers **8–10** are stable up to 300 °C [11] and hence cannot be the precursors of dimers **1** and **5** at 150 °C [reaction (1)]. The same is also true for trimer **7** which is stable up to 250 °C [11].

Thus, the formation of dimers **1** and **5** as secondary products in reaction (1) can only be related to the thermal transformations of dimers **3** and **4**.

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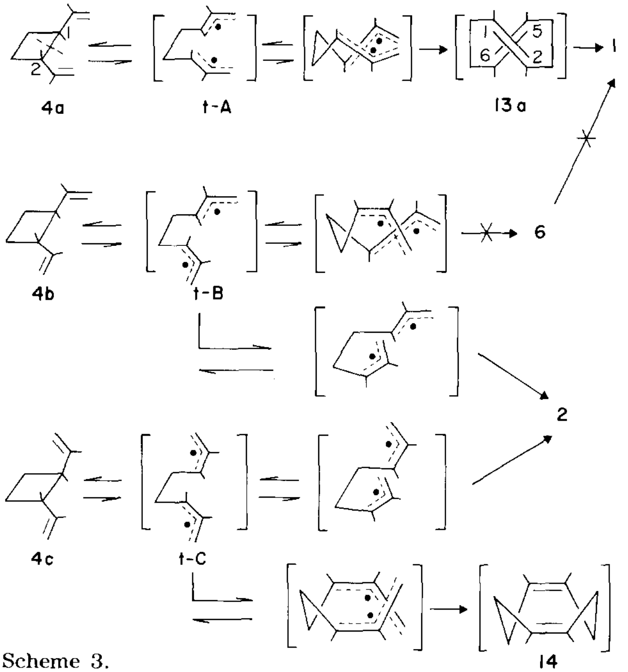
*Ratio calculated on the basis of reaction (1) and data in ref. 11.

trans-F-Divinylcyclobutane (**4**) has proved to be stable up to 165 °C whilst its *cis* isomer **3** is unstable at temperatures as low as 135 °C.

The thermal reactions of cyclodimer 4

Dimer **4** is isomerized quantitatively when heated (50 h at 200 °C), to yield two products (dimers **1** and **2**) in a 11:1 ratio [Scheme 1, reaction (3)]. The analogous thermal reaction of *trans*-divinylcyclobutane does not yield the hydrogen analogue of dimer **1**, but rather the analogues of dimers **2** and **3**, as well as *cis,cis*-1,5-cyclo-octadiene and butadiene [12]. The hydrogen analogue of **1** has been obtained previously by the photolysis of *cis,cis*-1,5-cyclo-octadiene sensitized by mercury [13], as well as by UV-irradiation of *trans,trans*-1,5-cyclo-octadiene [14].

In spite of the fact that no intermediates were observed (^{19}F NMR spectroscopy) in reaction (3), it seems reasonable to assume that dimer **1** might also be generated in this case from the unstable *cis,trans*- or *trans,trans*-*F*-1,5-cyclo-octadiene, formed from dimer **4** via a Cope reaction. However, although a concerted thermal Cope reaction is symmetry-allowed, it is impossible sterically as far as *trans-F*-divinylcyclobutane (**4**) is concerned. Nevertheless, this does not exclude the possibility that the reaction proceeds by a stepwise mechanism (cf. ref. 12). Indeed, in the case of reaction (3) a stepwise mechanism is confirmed by the coformation of dimer **2**. The process may be described as of the $[_{\sigma}2+_{\pi}2]$ type, implying an initial C(1)–C(2) bond breakage which results in the formation of bis-allyl intermediates, **t-(A–C)** (see Scheme 3).

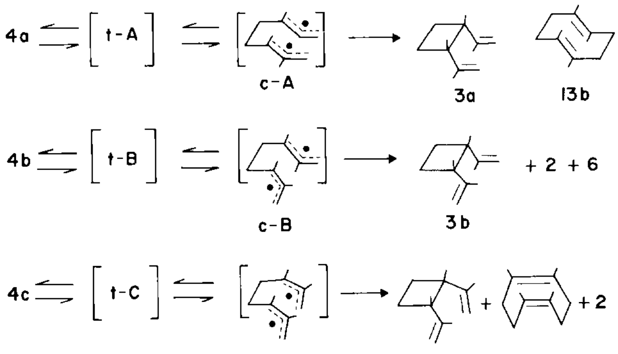


Scheme 3.

Since rotation within the allyl radical is known to be hindered, the ultimate result of a C(1)–C(2) bond-breaking reaction must depend upon the conformation of molecule **4** at the time the bond is broken. In other words, different conformers **4(a–c)** must produce biradicals **t-(A–C)** which differ in the structure of the allyl fragments (Scheme 3). As a result of the rotation of ordinary C–C bonds, the biradicals **t-(A–C)** may adopt conformations which are convenient for eight-, six- and four-membered ring closure and which yield the *F*-cyclo-octadienes **6**, **13a*** and **14**, *F*-vinylcyclohexene (**2**) (Scheme 3) and *cis-F*-divinylcyclobutane (**3**) (Scheme 4) as products. Additionally, there is also the possibility that such biradicals may decay into two diene molecules (cf. ref. 12), but this does not appear to be the case for biradicals of the type **t-(A–C)** since *F*-butadiene is absent from among the products of reaction (3). Later we shall retrace the fate of each of the **t-(A–C)** biradicals and demonstrate the possibilities which arise in the thermal reactions of dimer **4**.

Biradical **t-A**, which is produced from the most stable conformer of dimer **4** (Scheme 3), cannot cyclize to *F*-vinylcyclohexene (**2**) without rotation at the allylic site, so cyclization would inevitably result in the initial **4a** or *trans,trans-F*-cyclo-octadiene (**13a**) which is unstable under the conditions of reaction (3) (cf. ref. 14). Since thermal concerted $[2_s+2_s]$-cycloaddition is forbidden while the allowed $[2_s+2_a]$ process for dimer **13a** is sterically impossible, it is obvious that intramolecular [2+2]-cycloaddition can only be achieved via a stepwise mechanism. Incidentally, examination of molecular models shows that two *trans* C=C bonds brought together as in molecule **13a** are situated in such a manner relative to each other that new σ bonds can only be formed between C-1 and C-5 atoms and between C-2 and C-6 atoms, resulting in the formation of the *F*-tricyclo-octane (**1**) structure.

The rearrangement **4**→**2** [Scheme 3, reaction (3)] requires that the biradical intermediate contains at least one *cis*-allyl group, as occurs in the biradical **t-B**, which must be derived from the less-stable conformer **4b**. In contrast to the biradical **t-A**, **t-B** is capable of stabilization in three ways:



Scheme 4.

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trans,trans-F-1,5-Cyclo-octadiene can exist in two forms: racemic (**13a**) and meso (**13b**).

(i) ring closure to the initial **4b**; (ii) ring closure to *F*-vinylcyclohexene (**2**); or (iii) ring closure to *cis,trans*-cyclo-octadiene (**6**), the latter being capable of a concerted thermal $[2_s+2_a]$-cycloaddition, i.e. **6** → **1**, which is allowed and feasible sterically. However, as will be shown below, the only product of the thermal reaction of dimer **6** is a polymer which is absent from the products of reaction (3). Hence, ring closure to dimer **2** appears to be the more preferable of the two ways of stabilizing biradical **t-B**, yielding the observed products.

As far as biradical **t-C** is concerned, there are also three ways of achieving stabilization; one leads to dimer **4c**, another to dimer **2** and the third to *cis,cis-F*-cyclo-octadiene (**14**) which is more stable than its corresponding *cis,trans*-**6** and *trans,trans*-**13a** isomers (Scheme 3). Indeed, reaction (3) generates a product which is stable at 200 °C, whose ^{19}F NMR spectrum does not contradict the structure of dimer **14**. However, the yields of this product are negligibly small (*c*. 0.5%) suggesting either that the biradical **t-C** is mainly stabilized by cyclization to the dimer **2** or to the conformer **4c** or the biradical **t-C**, which because of its instability takes virtually no part in reaction (3) (cf. ref. 5).

Since the hydrogen analogue of dimer **4** is capable of isomerization to *cis*-divinylcyclobutane [5, 12], the possibility of stabilization of the type **t-(A–C)** → **3** should also be considered (Scheme 4). Cyclization of biradicals **t-(A–C)** to dimer **4** does not require rotation about C–C bonds and the process **4** ⇆ **t-(A–C)** is, apparently, reversible (Scheme 3). In contrast, the isomerization **4** → **3** requires rotation about the normal bonds in **t-(A–C)** to allow conversion of **t-(A–C)** biradicals into **c-(A–C)** biradicals, the latter being capable of cyclization to dimer **3** as well as to the *F*-cyclo-octadienes **6**, **13b** and **14**, and to dimer **2** (Scheme 4). Under the conditions of reaction (3), the *F*-cyclo-octadienes **6**, **13b** and **14** can produce *syn*-**5a** and *anti*-**5b** tricyclo-octanes and a polymer, none of which were found amongst the reaction products. In addition, the products of the thermal reaction of dimer **3** (see below) differ from the products of reaction (3), ruling out the possibility that the isomerization **4** → **3** makes an appreciable contribution to reaction (3).

The thermal transformations of dimer **4** at 200 °C explain its absence from amongst the products of reaction (2) (Scheme 1) and the appearance instead of significant quantities of dimers **1** and **2**. Dimer **4** is stable at 150 °C and hence cannot be the source of dimers **1** and **5** in reaction (1). For this reason, only *cis-F*-divinylcyclobutane (**3**) provides such an opportunity.

The thermal reactions of cyclodimer 3

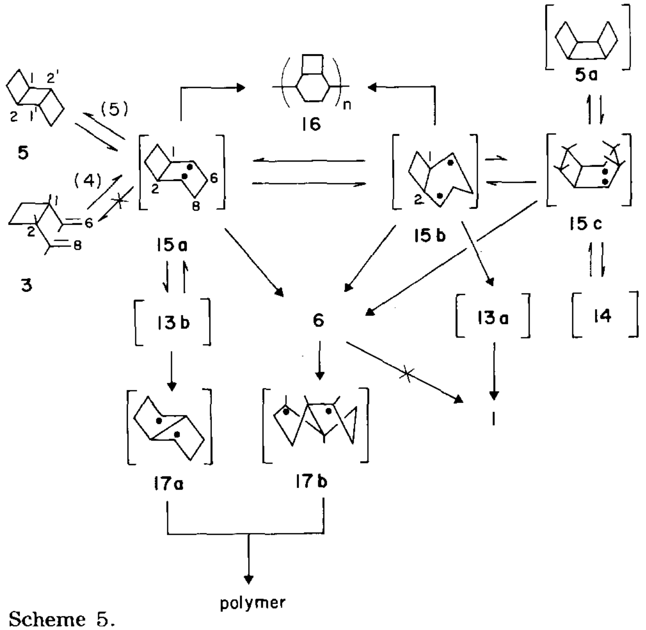
In contrast to its hydrogen analogue, which is isomerized to *cis,cis*-cyclo-octadiene [4, 5] at the instant of formation, dimer **3** is capable of isolation from the product mixture arising from reaction (1). However, at 150 °C it is slowly converted to dimers **1**, **5** and **6**, and to a polymer which are generated simultaneously [Scheme 1, reaction (4)]. It should be noted that the ratio **6**/polymer decreases with time while the ratio **1**/**5**/(**6** + polymer) remains nearly constant. An increase in the reaction temperature results (from 165 °C) in a sharp increase in the fraction of dimer **1** in the product mixture and a decrease in the fractions of dimers **5** and **6** with time. Such temperature dependence points to the instability of dimer **5**, apart from anything else. In fact, dimer **5** on its own when heated ($\geqslant 150$ °C) gives dimers **1** and **6**, as well as a polymer [reaction (5)]. The product ratio for reaction (5) also changes with time, which is consistent with the polymerization of dimer **6** [reaction (6)].

$$\mathbf{5} \longrightarrow \mathbf{1}+\mathbf{6}+\text{polymer} \qquad (5)$$

$$\mathbf{6} \longrightarrow \text{polymer} \qquad (6)$$

Polymer proved to be the sole product of the thermal reaction of dimer **6** both at room temperature and upon heating (150 °C). The absence of dimer **1** from the products of reaction (6) demonstrates that dimers **1** and **6** are not converted into each other [dimer **1** is stable up to 300 °C]. Hence, in reaction (5), dimer **1** can only be derived from dimer **5**.

The isomerization **5** → **1** [reaction (5)] suggests the breakage of two C–C bonds and the formation of other new C–C bonds. Because of steric reasons, such an isomerization cannot be a one-step concerted $[2_s+2_a]$ process and must therefore proceed via a stepwise mechanism with the biradical intermediate **15** being capable of existing as an equilibrium mixture of conformers **15(a–c)** (Scheme 5). Biradical **15** can be stabilized in several ways, e.g. inter- and intra-molecular recombination as well as bond-breaking involving C(1)–C(2) or C(6)–C(8) bonds. Polymer **16** may be the product of an intermolecular recombination of biradical **15** (Scheme 5, cf. ref. 15).



Scheme 5.

Intramolecular recombination of biradicals **15(a,c)** should yield the tricyclo-octanes **5** and **5a**. It should be noted that the formation of conformer **15c** must be extremely unfavourable owing to repulsion between the axial fluorine atoms and the fact that the equilibrium **5** ⇆ **5a** is virtually completely shifted towards **5** [**5a** was not present in the products of reaction (5)] (cf. ref. 15). Bond breakage of the type C(6)–C(8) is excluded for biradical **15** since dimer **3** was also not found amongst the products of reaction (5) (Scheme 5, cf. ref. 15).

Bond breaking between C-1 and C-2 can be conrotatory or disrotatory and in the case of biradicals **15(a–c)** yields different products. Thus, conrotatory breakage of biradical **15a** involving the C(1)–C(2) bond should yield *cis,trans-F*-cyclo-octadiene (**6**), while disrotatory breakage may result in the formation of unstable *meso-trans,trans-F*-cyclo-octadiene (**13b**). It should be noted that dimer **13b** is not capable of thermal isomerization to dimer **1** for steric reasons. Under the conditions of reaction (5), it may give rise to the biradicals **15a** and **17a**, which are shown together with hypothetical ways for their stabilization in Scheme 5.

Conrotatory breakage of the C(1)–C(2) bond in biradical **15c** would lead to *F*-cyclo-octadiene (**6**). Disrotatory breakage is excluded since the expected *cis,cis-F*-cyclo-octadiene (**14**) does not appear amongst the products of reaction (5) (cf. ref. 15).

Disrotatory breakage of the C(1)–C(2) bond in biradical **15b** must result in the formation of *cis,trans-F*-cyclo-octadiene (**6**), while conrotatory breakage would yield racemic *trans,trans-F*-cyclo-octadiene (**13a**).

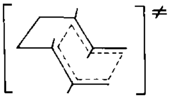
In fact, the electron density distribution in the *F*-tricyclo-octane molecule **5** (see below) may be interpreted as a contribution of the π component in the C(1)–C(2′) and C(2)–C(1′) bonds (Scheme 5) and, hence, as a result of a partial cyclo-octadiene character in this molecule. Free-state geometrical calculations for the molecule show that the breakage of two C(1)–C(2) bonds would most probably result in the formation of *F*-cyclo-octadiene (**6**) having torsion angles of $\phi_1 = 0°$ and $\phi_2 = 131°$ for the C=C bonds. The inability of dimer **6** to undergo the allowed concerted $[2_s + 2_a]$-cycloaddition, **6** → **1**, and the ease with which it polymerizes [reaction (6)] may be related to the biradical character of the 'twisted' *trans* bond in the molecule.

Thus, the formation of dimer **1** observed in reaction (5) cannot be explained by the isomerizations of the *F*-cyclo-octadienes **6** and **13b** (see above). Hence, it must be assumed that C(1)–C(2) bond breakage in biradical **15** occurs in a conrotatory fashion, which, in turn, results in the formation of dimer **6** as well as *F*-cyclo-octadiene (**13a**). The latter is capable of being isomerized to dimer **1**, as has been shown above (Scheme 3).

Having considered the formation of dimers **1** and **6** and polymer in reactions (5) and (6) (see above), one must now return to reaction (4), i.e. **3** → **5** + **1** + **6** + polymer, to discuss their mutual relationships. The transformations of dimer **3** [reaction (4)] can be interpreted as being a combination of three consecutive steps, involving the intramolecular [2 + 2]-cycloaddition **3** → **5**, followed by the isomerization **5** → **1** + **6** [reaction (5)] and then by the polymerization of **6** [reaction (6)]. However, because of the impossibility of separating the first two steps [dimers **5**, **1** and **6** are always formed simultaneously], such an interpretation is unacceptable. Hence, in order to explain all the observed facts, the possible thermal reactions of dimer **3** are considered below. They may include the isomerization **3**→**4**, a concerted or stepwise Cope rearrangement and the [2+2]-cycloaddition **3**→**5**.

The isomerization **3**→**4** occurs as a stepwise process involving the formation of the bis-allyl biradicals **c-(A–C)** as a result of initial C(1)–C(2) bond breakage, then rotation around normal bonds leading to the biradical intermediates **t-(A–C)** (Schemes 3 and 6). Stabilization of the latter must yield dimers **1**, **2** and **14** together with dimer **4**. The absence of dimers **2**, **4** and **14** from amongst the products of reaction (4) does not exclude the isomerization **3**→**4** completely but makes its appreciable contribution at 150 °C somewhat improbable.

An allowed concerted Cope rearrangement would inevitably proceed via the chair-type transition state **19** [6] and yield in the case of *F*-divinylcyclobutane (**3**) the *cis,cis-F*-cyclo-octadiene **14** which is not detected amongst the products of reaction (4).



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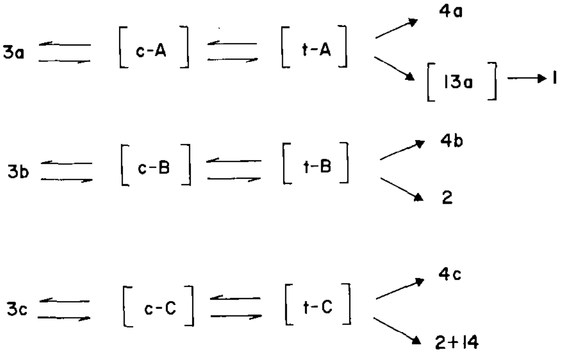
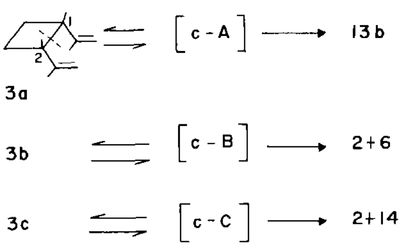
The stepwise Cope rearrangement which starts with C(1)–C(2) bond breakage in the cyclic molecule must proceed via the bis-allyl biradical intermediates **c-(A–C)** (Scheme 7) and yield the *F*-cyclo-octadienes **6**, **13b** and **14**, as well as dimer **2** which is not formed in reaction (4).

It seems reasonable, therefore, to assume that concerted reactions and stepwise processes, starting from cyclic C(1)–C(2) bond breakage, do not play a dominant role in the thermal transformations of dimer **3** at 150 °C.



Scheme 6.



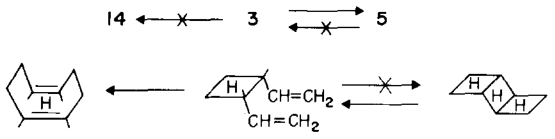
Scheme 7.

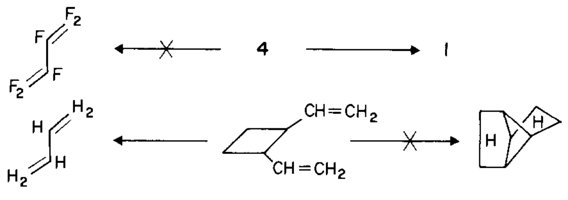
Reactions which start with C(6)–C(8) bond formation may be considered as alternative processes (Scheme 5). The [2 + 2]-cycloaddition **3** → **5** may be considered as one such reaction. However, because of steric considerations, intramolecular [2 + 2]-cycloaddition involving dimer **3** can only proceed as a stepwise process involving the biradical intermediate **15** (Scheme 5).

The fact that heating dimer **3** [reaction (4)] results in the simultaneous formation of *F*-tricyclo-octane (**5**) and its transformation products indicates the existence of the equilibrium **5** ⇆ **15**. On the other hand, the absence of dimer **3** from amongst the isomerization products of dimer **5** [reaction (5)] provides evidence for the irreversibility of the isomerization **3** → **5** + **6** [Scheme 5, reaction (4)]. Theoretically, reaction (4) can be divided into two: an isomerization **3** → **5** which occurs as a [2 + 2]-cycloaddition process and an isomerization **3** → **6** as a competing stepwise Cope reaction. Both processes start with C(6)–C(8) bond formation and proceed via the intermediate **15**, which is common to dimers **5** and **6** and for reactions (4) and (5) (Scheme 5). In the actual reaction, the existence of the above-mentioned equilibrium and its shift due to the irreversible stabilizations of biradical **15** (**15** → **6** → polymer and **15** → **13a** → **1**) would have a twofold effect. First, it would lead to the simultaneous formation of all the products of reaction (4) and, secondly, it would make a deliberate change of the product ratios [in favour of dimers **5** or **6**, for example] impossible.

Hence, it appears that this is the only possible interpretation consistent with all the observed facts. It should be noted, however, that the mechanism depicted in Scheme 5 reflects only those processes which proceed at 150 °C. At higher temperatures (⩾165 °C), due to C(1)–C(2) bond breakage, the participation of the competing reactions **3** → **4** and **3** → **1** + **2** is possible up to their predominance, as occurs for dimer **4** [reaction (3)].

In conclusion, it should be stated that the behaviour of dimers **3** and **5**, as well as of dimer **4**, in thermal reactions is quite different from that of their hydrogen analogues [4, 5, 12].





Most of the various distinctions (see above) are readily explained by the rule that a fluoro-organic compound is more stable, the fewer F atoms it has attached to the multiple bonds.

Spectral characteristics and proofs of structures

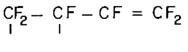
The pure dimers **1–5** were isolated by preparative GLC methods, the tricyclo-octane (**5**) being obtained after bromination of the dimer mixture. The unstable dimer **6** was not isolated in the pure state. The sample which was closest to purity obtained immediately after preparative GLC contained ~15% of dimer **4** (^{19}F NMR spectroscopy). In contrast to dimer **4**, dimer **6** was found to give a 2:1 complex with rhodium dicarbonyl acetylacetonate under mild conditions (20 °C). This enabled the isolation of dimer **6** as the stable derivative **12**. The elemental analyses of adducts as well as their mass spectra show that all of these were *F*-butadiene dimers.

4-Trifluorovinyl-nonafluorocyclohexene (2)

The ^{19}F NMR spectrum of the dimer involves 12 signals arising from different fluorine atoms, three of which (F(1)–F(3)) are characteristic of the trifluorovinyl group, six others (geminal in pairs) are associated with three CF_2 groups, one other (F(4)) is attached to the tertiary C atom while the last two (F(7) and F(8)) are attached to the C=C bond, as confirmed by their chemical shifts (104.6, 78.5 and 77.0 ppm, respectively). The presence of only one trifluorovinyl group together with the absence of CF_3 groups excludes any non-cyclic structure, while the non-equivalence of all the F atoms suggests an asymmetric cyclic molecule. The observed equivalence of the J(F–F) constants, $J(5–6)=J(9–10)$, $J(5–7)=J(9–8)$, $J(5–8)=J(9–7)$, $J(6–7)=J(10–8)$ and $J(6–8)=J(10–7)$, in the dimer spectrum is consistent only with a $-CF_2CF=CFCF_2-$ fragment, leaving a molecule which contains CF and $CF=CF_2$ groups as the sole possible structure **2** in which equivalent F atoms do not occur. Structure **2** is also confirmed by vibrational spectral data. The Raman spectrum of the dimer contains an intense polarized $\nu(C=C)$ band at a frequency of 1785 cm^{-1} (1783 cm^{-1} in the IR spectrum) and a polarized band of medium intensity at 1752 cm^{-1} (1749 cm^{-1} in the IR spectrum), which may be attributed to the $\nu(C=C)$ band arising from the $-CF=CF-$ site of a six-membered cycle (cf. 1749 cm^{-1} in the IR spectrum of *F*-cyclohexene [16]).

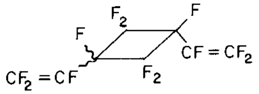
cis- *and* trans-*1,2-Bis(trifluorovinyl)-1,2,3,3,4,4-hexafluorocyclobutanes (3) and (4)*

Each of the two ^{19}F NMR spectra of the C_8F_{12} dimers contains six signals of equal intensity. Two of these signals correspond to geminal F atoms and form an AB-system, three others are characteristic of the trifluorovinyl group and one other corresponds to the F atoms attached to the tertiary C atoms. Such a spectrum is in accordance with fragment **D** (see below). The equivalence within each of the six pairs of 12 F atoms shows that each molecule contains two halves of type **D**. The same equivalence limits the possible variants adopted by the structures **3**, **3a**, **4** and **4a**.



$\underset{|}{CF_2}-\underset{|}{CF}-CF=CF_2$

D



3A - cis

4A - trans

All these structures assume the equivalence of pairs of C atoms and, hence, the presence of a 'half' set of signals in ^{13}C NMR spectrum. Indeed, the spectrum of dimer **4–4a** contains four instead of eight signals, two corresponding to C atoms associated with $-CF{=}CF_2$ groups, and the other two signals being associated with tertiary and secondary C atoms bonded to one and to two F atoms, respectively. The presence of trifluorovinyl groups in molecules **3–3a** and **4–4a** is confirmed by the vibrational spectral data (intensely polarized bands at 1784 cm^{-1} in the Raman spectra and intense bands at 1788 and 1785 cm^{-1} in the IR spectra). The spectral data, however, do not enable a choice to be made between structures **3–3a** and **4–4a**. Such a choice in favour of structures **3** and **4** is based on the chemical transformations of these dimers. For example, dimers **3a** and **4a** (cf. ref. 17), in contrast to their structural isomers **3** and **4**, cannot give rise to *F*-tricyclo-octanes on heating. This excludes structures **3a** and **4a**, and also indicates that dimers **3** and **4** are steric but not structural isomers. The same transformations enable the *cis* structure to be ascribed to the less stable isomer **3** which yields *F*-tricyclo-octane (**5**) on heating, and the *trans* structure to the more stable isomer **4**.

anti-*Dodecafluorotricyclo[4.2.0.0.^{2,5}]octane (5)*

The structure of dimer **5** has been demonstrated by X-ray analysis. The tricyclo-octane skeleton of molecule **5** has a chair conformation (Fig. 1).

Because the molecule has central symmetry, the centre cycle is ideally planar and the C(1)–C(4) and C(1')–C(4') atoms of the side cycles are coplanar to within ±0.005(1) Å. The dihedral angle between adjacent four-membered cycles is equal to 115.1(1)°. The C–C bond lengths have the expected values, similar to those found earlier in tricyclo[4.2.0.0^{2,5}] derivatives [18–20]. In *F*-tricyclo-octane (**5**), the C(1)–C(2) bond increases up to 1.611(1) Å and a small decrease in the C(1)–C(2') [and in the C(1')–C(2)] bond to 1.524(1) Å is observed, compared with the average C–C bond length of 1.557 Å found in the hydrogen analogue of **5** by gaseous electron diffraction

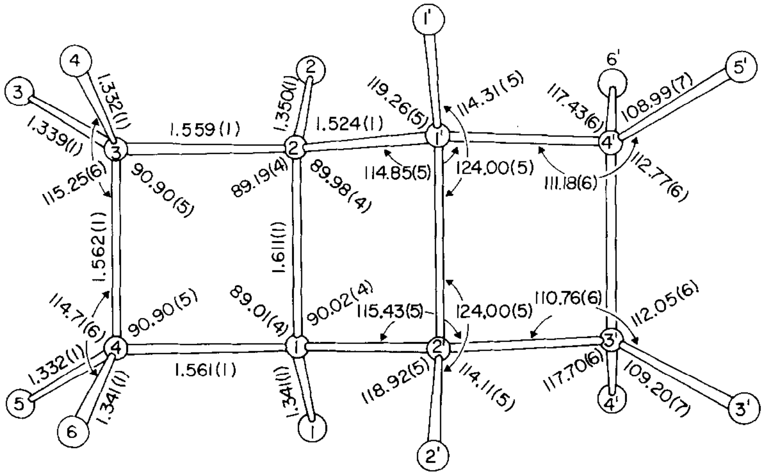


Fig. 1. A general view of the *F*-tricyclo[4.2.0.0^{2,5}]octane (**5**) molecule.

methods [21]. The other C–C bond lengths in molecule **5** are equal, their average value being equal to 1.561(1) Å, while the C–F bond lengths are of the usual value [22]. The orientation of the fluorine atoms relative to the carbon skeleton of molecule **5** is characterized by the following torsion angle values: F(1)–C(1)–C(2)–F(2), −0.47(9); F(1)–C(1)–C(2')–F(2), −100.44(8); F(1)–C(1)–C(4)–F(5), −11.8(1); F(1)–C(1)–C(4)–F(6), 114.7(1); F(2)–C(2)–C(3)–F(3), 13.9(1); F(2)–C(2)–C(3)–F(4), −112.8(1); F(3)–C(3)–C(4)–F(5), −1.2(1); F(3)–C(3)–C(4)–F(6), −126.8(1); F(4)–C(3)–C(4)–F(5), 124.5(1); and F(4)–C(3)–C(4)–F(6), −1.1(1)°. The intramolecular non-bonding distances F(4)...F(1') of 2.674(1) Å and F(6)...F(2') of 2.637(1) Å are shortened relative to the sum of the van der Waals' radii for F atoms (~2.8 Å) [23]. Calculation of the geometry of molecule **5** in the free state by the method of molecular mechanics, using the observed X-ray diffraction data as a zero approximation, correctly reproduces its peculiarities, viz. a planar structure consisting of four-membered cycles with a maximum value for the C(1)–C(2) bond lengths (1.590 Å versus 1.546–1.549 Å for the other virtually equalized C–C bonds). However, this calculation underestimates the values of the C–C bond lengths in the peripheral cycles by 0.012–0.016 Å and overestimates the C(1)–C(2') (C(1')–C(2)) bond lengths in the central cycle by 0.024 Å. The calculated bond angle C(4)–C(1)–C(2') (characterizing the bonding of the planes of the adjacent cycles and which is equal to 122.7°) is also much greater than the experimental value (115.1°). These discrepancies in the geometrical parameters may be the result of imperfections in the parametrization of the MM2 program, which disregard the electronic effects of the electronegative F atoms and the rehybridization of the orbitals in the C atoms, and which lead to a significant deviation in the bond angles from the ideal 'tetrahedral' values. Figure 2(a, b) represents sections of the deformation electron density (DED) in the plane

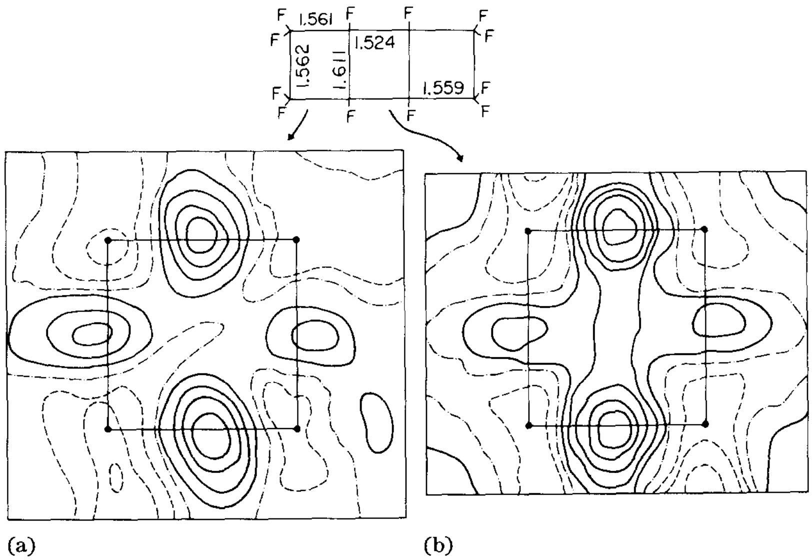


Fig. 2. Deformation electron density sections for cyclobutane fragments of tricyclo-octane (**5**): (a) peripheral cycle; (b) central cycle. Interval between isolines, 0.1 e Å^{-3}.

of the cyclobutane fragments. Such maps allow a judgement to be made of the character of the electron density redistribution during the formation of chemical bonds between the atoms [24, 25]. A characteristic feature of the DED in Fig. 2 is the presence of distinct maxima of the positive electron density at the centre of the C–C bonds. The heights of these maxima correlate with the C–C bond lengths and are as follows: C(1)–C(2) bond, 0.25; C(1)–C(4) and C(2)–C(3) bonds, 0.40; C(3)–C(4) bond, 0.30; and C(1)–C(2′) bond, 0.50 e Å^{-3}. What should be stressed is that the centres of positive DED are shifted from lines interconnecting the nuclei of the C atoms to points 'external' to the four-membered cycles by distances of up to *c*. 0.15 Å, thus providing experimental confirmation for existing ideas regarding the formation of bent bonds in small cycles, including cyclobutane derivatives. Similar values of the heights and shifts in DED maxima for ordinary C–C bonds in four-membered cycles have also been reported for 1,2-dihydro- and 1,2,4,5-tetrahydrocyclobutabenzenes [26].

Figure 3 depicts the DED section perpendicular to the central cycle plane, which passes through the C(1) and C(2′) atoms of molecule **5**. A peculiar feature of this section is a noticeable elongation of the DED maximum normal to the bond line, indicating the presence of a π component and, hence, the partial cyclo-octadiene character of molecule **5**. A decrease in the C(1)–C(2′) bond length to 1.524(1) Å and the chemical shift of the F atoms in the central cycle [112.5 ppm relative to 141 ppm for the corresponding F atoms in *F*-tricyclo-octane (**1**)] also provide evidence for the partial double bond character of the linkage between the C(1) and C(2′) atoms.

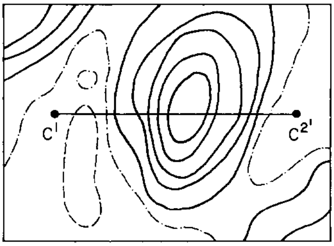
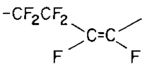


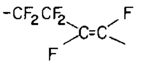
Fig. 3. Deformation electron density section for the central cycle of *F*-tricyclo-octane (**5**), normal to the plane through the C(1) and C(2') atoms. Interval between isolines, 0.1 e Å^{-3}.

cis,trans-*Dodecafluoro-1,5-cyclo-octadiene (6)*

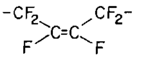
The ^{19}F NMR spectrum of the dimer involves seven signals with different intensities, i.e. a non-first-order spectrum. None of the signals, which are located within the range 25–65 ppm, correspond to the F atoms of the trifluorovinyl or trifluoromethyl groups. The width of the lines in the spectrum is 60–500 Hz. In contrast, the ^{13}C NMR spectrum consists of two multiplets of equal integral intensity. One multiplet corresponds to the C atoms which are directly bonded to one F atom and located in –CF=CF– groups, as confirmed by the chemical shift (145 ppm) and by the coupling constant $J(C–F) = 274$ Hz. The second multiplet, with a chemical shift of 110 ppm and a triplet coupling constant $J(C–F_2) = 274$ Hz, corresponds to the carbon atoms of the CF_2 groups.



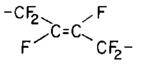
cis-E



trans-E



cis-F



trans-F

The absence of other signals in the ^{13}C NMR spectrum indicates that the dimer molecule can only include **E** and **F** fragments and their combinations, as for the *F*-cyclo-octadienes **6**, **6(a,b)**, **13(a,b)** and **14**.

6

6a

6b

13a 13b 14

It was shown earlier that the mass spectra of non-fluorinated 1,3-, 1,4- and 1,5-cyclo-octadienes are very similar but with one important distinction, i.e. 1,3- and 1,4-cyclo-octadienes give peaks at $\frac{1}{2}M^+$ with a low intensity, while the peaks at $\frac{1}{2}M^+$ in the spectra of the 1,5-cyclo-octadienes have a maximum intensity [14]. If this rule also applies in the mass spectra of the *F*-cyclo-octadienes, then the peak with a mass of 162 and an intensity of 100% observed in the dimer spectrum excludes structures **6(a,b)** and suggests a 1,5-structure for *F*-cyclo-octadiene. Molecules of the *F*-1,5-cyclo-octadienes **13(a,b)** and **14**, which have an axis or plane of symmetry, must exhibit simple ^{19}F NMR spectra containing two (1:2) or three (1:1:1) signals of fourfold equivalent –CF= and CF_2 groups, contradicting the observed dimer spectrum. The vibrational spectra (for C_8F_{12} molecules) favour a monocyclic structure with two separate C=C bonds. The Raman spectrum contains intense polarized bands corresponding to ν(C=C) with frequencies at 1681 and 1670 cm^{-1}. As far as the IR spectrum is concerned, only a band of medium intensity with a frequency of 1668 cm^{-1} was observed. It is notable that the frequencies of both ν(C=C) vibrations are diminished relative to the ν(C=C) frequency at 1720 cm^{-1} in the *F*-cyclo-octene spectrum [27]. Such a decrease is feasible for structure **6b** because of bond conjugation. However, the expected difference between the frequencies of the symmetric ν_s and antisymmetric ν_{as} vibrations should have been more than that observed (11 cm^{-1}), and one of the bands in the Raman spectrum corresponding to ν_{as} should have been depolarized. The presence of two polarized ν(C=C) bands in the Raman spectrum suggests the absence of any interaction between the C=C bonds in the dimer molecule thus excluding structure **6b**. On the other hand, the existence of only one ν(C=C) vibration in the IR spectrum demonstrates centrosymmetric substitution of one of the two C=C bonds. Since the centrosymmetry of the C=C bond presupposes a *trans* arrangement of identical subsituents at either end of the bond, structures **6(a,b)** and **14** are excluded, as are structures **13(a,b)** since they contain two centrosymmetric C=C bonds rather than one. Hence, only structure **6** for *cis,trans-F*-1,5-cyclo-octadiene is consistent with the whole range of mass, IR, Raman and NMR spectral data for the dimer.

The correctness of this conclusion has been confirmed by an X-ray analysis of the 2:1 complex **12**, formed between dimer **6** and rhodium dicarbonyl acetylacetonate (Fig. 4). In this complex the *F*-1,5-cyclo-octadiene molecule is in η^2-type coordination and is characterized by values for the torsion angles C(4)–C(5)–C(6)–C(7) (ϕ_1) and C(8)–C(1)–C(2)–C(3) (ϕ_2) of 0.8(9)° and 108.0(9)°, respectively, i.e. indicating a *cis,trans* configuration. The torsion angles F(1)–C(1)–C(2)–F(2) and F(5)–C(5)–C(6)–F(6), characterizing double-bond twist, have respective values of −152.4(7)° and −0.3(5)°. Because the C(1)=C(2) bond in molecule **12** is both twisted significantly and coordinated with the Rh atom, a significant lengthening of this bond to 1.469(9) Å was observed. It should be pointed out that in comparison the lengths of the two other non-coordinated bonds of the cyclo-octadienyl ligands in molecule **12**, i.e. C(5)=C(6) and C(19)=C(20), were 1.31(1) and 1.29(1) Å, respectively, being characteristic of bonds of this type with fluorine substituents [18].

Due to $[_{\pi}2+(_{\sigma}2+_{\pi}2)]$-cycloaddition involving participation of the acetylacetonate ligand of the initial rhodium complex, the second *F*-1,5-cyclo-octadiene molecule forms a metallacyclic system with an Rh–C(16) σ bond of length 2.201(6) Å. The ordinary bonds C(11)–C(15) and C(15)–C(16) had lengths of 1.579(9) and 1.550(9) Å, respectively. The torsion angles C(18)–C(19)–C(20)–C(21) and F(19)–C(19)–C(20)–F(20) in molecule **12** were 2.1(9) and −1.9(5)°, respectively, with angles C(22)–C(15)–C(16)–C(17) and F(15)–C(15)–C(16)–F(16) being −94.7(8) and −141.6(7)°, respectively, which again confirms the *cis,trans* configuration of the initial *F*-1,5-cyclo-octadiene. The rhodium atom was characterized by a distorted octahedral

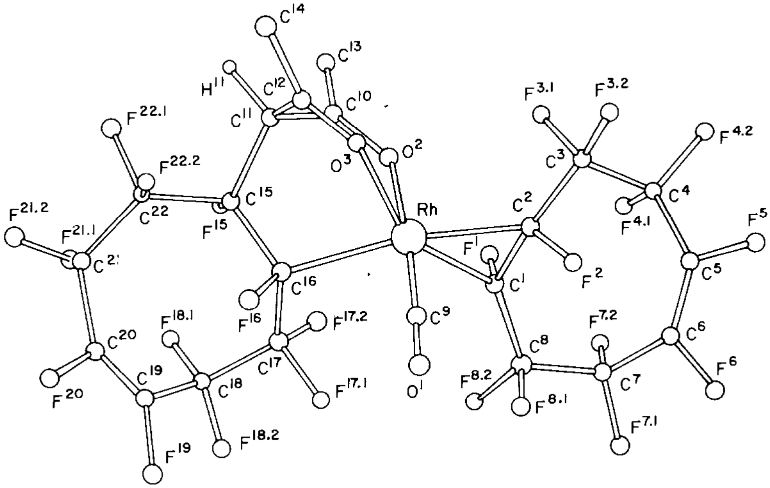


Fig. 4. A general view of molecule **12**. The most important geometrical parameters of the molecule are as follows. Bond lengths: Rh–C(1), 2.049(6); Rh–C(2), 2.072(6); Rh–O(2), 2.073(4); Rh–O(3), 2.193(4); Rh–C(9), 1.840(6); Rh–C(16), 2.201(6); C(1)–C(2), 1.469(9); C(5)–C(6), 1.313(9); C(15)–C(16), 1.550(9); C(19)–C(20), 1.289(9); O(1)–C(9), 1.138(8); O(2)–C(10), 1.222(7); O(3)–C(12), 1.214(8) Å. Bond angles: C(1)–Rh–C(2), 41.8(2); C(1)–Rh–C(16), 124.6(2); C(2)–Rh–C(16), 166.3(2); O(2)–Rh–C(9); 175.1(2); O(3)–Rh–C(9), 93.0(2); Rh–C(9)–O(1), 176.0(6); C(8)–C(1)–C(2), 123.0(5); C(1)–C(2)–C(3), 121.8(5)°.

coordination involving Rh–C(1) and Rh–C(2) distances of 2.049(6) and 2.072(6) Å, respectively, i.e. slightly shorter than the Rh–C(16) σ bond. The lengths of the coordination bonds Rh–O(2,3) were similar, being equal to 2.073(4) and 2.193(4) Å, while the corresponding bonds C(10)–O(2) and C(12)–O(3) had lengths of 1.222(7) and 1.214(8) Å indicating their double-bond character (Fig. 4). Thus, the unstable product of the isomerization of dimers **3** and **5**, which is capable of spontaneous polymerization and complex formation with rhodium dicarbonyl acetylacetonate, possesses the same structure as *cis,trans-F*-1,5-cyclo-octadiene (**6**).

Experimental

Mass spectra were recorded on a VG 7070E spectrometer employing an ionizing electron energy of 70 eV, an ionic source temperature of 90 °C and a lap system of 30 °C. The results are given in terms of *m*/*z*, (% intensity), [tentative assignment]. IR spectra over the range 400–4000 cm^{-1} were measured as a thin layer on an UR-20 spectrophotometer, while Raman spectra over the range 10–4000 cm^{-1} were measured on a Ramanor HG-2S spectrometer using 100 mW power Ar^+ laser excitation at the 5145 Å spectral band. ^{19}F and ^{13}C NMR spectra were recorded on a Bruker WP-200 SY spectrometer (working frequencies of 188.3 and 51.31 MHz, respectively) in deuteroacetone or carbon tetrachloride. Chemical shifts (in ppm) are quoted relative to external trifluoroacetic acid ($-\delta_F$) and tetramethylsilane (δ_C). Mathematical narrowing of the peaks was used in the primary treatment of the spectra.

All X-ray calculations were performed on an Eclipse S/200 computer using an INEXTL program [28]. Analysis of the anisotropic thermal parameters in the crystal of molecule **5** was carried out using the rigid-body LTS model [29]. Calculations of the optimized geometry of molecule **5** were undertaken on an ES-1060 computer using the MM2 program [30] and the Meyer force-field variant [31] for the analysis of fluorine-containing compounds. All calculations and analysis of the deformation electron density maps were performed according to methods described by Hall [24].

Separation and purification of the products were achieved via a preparative GLC method [Tzvet 4-67 chromatograph with catharometer detector, 4000 × 13 mm column, Craitex (25%) on Chromaton W carrier, helium as the carrier gas and column temperatures of 40 and 100 °C].

The thermal reactions of hexafluoro-1,3-butadiene

Reaction (1), Scheme 1

F-Butadiene (72 g) was heated in a stainless-steel bomb at 150 °C for 120 h*. The following fractions were distilled from the reaction mixture: (a) *F*-butadiene (b.p., 5–10 °C, 10 g); (b) dimer **1** (b.p., 63–85 °C, 0.5 g); (c) dimers **3**, **4** and **5** (in a 27:66:7 ratio) along with unidentified impurities (b.p., 90–110 °C, 37.7 g); and (d) a mixture of trimers **7**–**10** [ratio **7**/(**8**+**9**)/**10**=1.1:5.8:1] (b.p., 165–185 °C, 16.1 g). The residue left amounted to 5 g. The conversion of *F*-butadiene was 86%. Yields (%): dimer **1**, 0.8; dimer **3**, 14; dimer **4**, 34; dimer **5**, 4; trimer **7**, 3.6; trimers **8**+**9**, 19; and trimer **10**, 3.2 (^{19}F NMR, GLC methods). Unidentified impurities amounted to *c*. 4%.

Reaction (2), Scheme 1

F-Butadiene (105.6 g) was heated in a stainless-steel bomb at 300 °C for 64 h. The following fractions were distilled from the reaction mixture: (a) *F*-cyclobutene (b.p., 5–10 °C, 51 g (47%)); (b) dimer **1** (b.p., 80–85 °C, 20.5 g (19.4%)); (c) dimer **2** (b.p., 87–103 °C, 9.9 g (9.5 %)); and (d) *F*-butadiene trimers (b.p., 148–195 °C, 13 g (12.3%)). The residue amounted to 4.7 g. The conversion of *F*-butadiene was 100%.

Dodecafluoro[3.3.0.0^{2,6}]octane (1)

This was obtained via the thermal reaction of *F*-butadiene at 300 °C (b.p., 80 °C) [8]. Mass spectrum: 324 (9) $[M]^+$; 305 (53) $[M-F]^+$; 255 (63) $[M-CF_3]^+$; 236 (15) $[M-CF_4]^+$; 224 (9) $[M-C_2F_4]^+$; 205 (100) $[M-C_2F_5]^+$; 186 (23) $[M-F-C_2F_5]^+$; 174 (11) $[M-C_3F_6]^+$; 162 (36) $[M-C_4F_6]^+$; 155 (38) $[M-CF_3-C_2F_4]^+$; 131 (23) $[M-F-C_5F_6]^+$; 124 (12) $[M-2C_2F_4]^+$; 117 (14) $[M-CF_4-C_2F_5]^+$; 93 (34) $[M-CF_3-C_4F_6]^+$; 69 (74) $[CF_3]^+$.

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*In all cases, oven temperatures are quoted.

*4-Trifluorovinyl-1,2,3,3,4,5,5,6,6-nonafluorocyclohexene (**2**)*

A mixture (14.5 g) of dimers **3** (13%) and **4** (87%) [isolated from the product mixture of reaction (1) using preparative GLC methods] was heated in a stainless-steel bomb at 280 °C for 30 h. The resulting mixture (10.7 g) containing *c.* 80% of **1** and 20% of **2** was distilled from the reaction products at 70–110 °C. A residue of 3.5 g remained. Pure dimer **2** (b.p., 100 °C) was isolated by preparative GLC methods. Mass spectrum: 324 (22) $[M]^+$; 305 (7) $[M-F]^+$; 255 (39) $[M-CF_3]^+$; 236 (10) $[M-CF_4]^+$; 224 (10) $[M-C_2F_4]^+$; 217 (7) $[M-F-CF_4]^+$; 205 (28) $[M-C_2F_5]^+$; 186 (15) $[M-2CF_3]^+$; 162 (100) $[M-C_4F_6]^+$; 131 (20) $[M-F-C_5F_6]^+$; 117 (12) $[M-3CF_3]^+$; 93 (49) $[M-C_4F_6-CF_3]^+$; 69 (41) $[CF_3]^+$. IR (cm^{-1}): 1783 (s); 1749 (m). Raman (cm^{-1}): 1785 (s, p)*; 1752 (m, p). ^{19}F NMR $-\delta$: 12.61 (dddd, F(1)); 30.6 (ddddddd, F(2)); 112.25 (dddddddd, F(3)); 104.63 (ddddddddd, F(4)); 33.76 (dddddddd, F(5)); 49.58 (dddddddd, F(6)); 78.45 (ddddddddd, F(7)); 77.07 (dddddd, F(8)); 30.14 (ddddddddddd, F(9)); 43.18 (ddddddddd, F(10)); 42.89 (ddddddd, F(11)); 55.53 (ddddddddd, F(12)) ppm. Coupling constants: *J*(1–2) 55.2; *J*(1–3), 40.7; *J*(1–9), 2.4; *J*(1–11), 2.4; *J*(2–3), 116.2; *J*(2–4), 40.7; *J*(2–6), 2.4; *J*(2–9), 8.4; *J*(2–10), 12.1; *J*(2–12), 6.2; *J*(3–4), 15; *J*(3–7), 1.8; *J*(3–9), 1.2; *J*(3–10), 12.8; *J*(3–11), 25.7; *J*(3–12), 6.4; *J*(4–5), 25.6; *J*(4–7), 4; *J*(4–8), 2.8; *J*(4–9), 4; *J*(4–10), 12.8; *J*(4–11), 6.4; *J*(4–12), 16.8; *J*(5–6), 290; *J*(5–7), 21.6; *J*(5–8), 9.9; *J*(5–9), 6; *J*(5–10), 2.1; *J*(5–11), 4; *J*(5–12), 9.9; *J*(6–7), 14.3; *J*(6–8), 16.9; *J*(6–9), 2.3; *J*(6–10), 2.3; *J*(6–11), 9.6; *J*(6–12), 9.9; *J*(7–8), 2.7; *J*(7–9), 10.5; *J*(7–10), 17.3; *J*(7–12), 9.2; *J*(7–9), 22.4; *J*(8–10), 13.6; *J*(9–10), 293; *J*(9–11), 21; *J*(9–12), 10.5; *J*(10–12), 2.5; *J*(11–12), 282 Hz. Analysis: Found: C, 29.45; F, 70.86%. C_8F_{12} requires: C, 29.63; F, 70.37%.

cis-*1,2-Bis(trifluorovinyl)-1,2,3,3,4,4-hexafluorocyclobutane (**3**)*

This was isolated from the mixture of *F*-butadiene dimers by preparative GLC methods (b.p., 94 °C). Mass spectrum: 324 (1.2) $[M]^+$; 255 (23) $[M-CF_3]^+$; 236 (9) $[M-CF_4]^+$; 224 (4) $[M-C_2F_4]^+$; 205 (12) $[M-C_2F_5]^+$; 186 (9) $[M-2CF_3]^+$; 162 (100) $[M-C_4F_6]^+$; 155 (17) $[M-C_2F_4-CF_3]^+$; 93 (51) $[M-C_4F_6-CF_3]^+$; 69 (25) $[CF_3]^+$. IR (cm^{-1}): 1782 (s). Raman (cm^{-1}): 1784 (vs). ^{19}F NMR $-\delta$: 15.67 (ddd, F(1)); 32.24 (dddd, F(2)); 113.28 (ddd, F(3)); 104.62 (dddd, F(4)); 47.78 and 53.86 (F(5) and F(6)), AB-system with additional coupling) ppm. Coupling constants: *J*(1–2), 57.5; *J*(1–3), 38.5; *J*(1–4), 6; *J*(2–3), 114.5; *J*(2–4), 29; *J*(2–?), 14; *J*(3–4), 25.5; *J*(4–?), 7; *J*(5–6), 225 Hz. Analysis: Found: C, 29.69; F, 70.50%. C_8F_{12} requires: C, 29.63; F, 70.37%.

trans-*1,2-Bis(trifluorovinyl)-1,2,3,3,4,4-hexafluorocyclobutane (**4**)*

The mixture (10 g) of dimers **4** (80%) and **3** (20%) was heated in a stainless-steel bomb at 200 °C for 2 h. A mixture (8 g) containing dimers **1** (2.7%), **2** (6%) and **4** (79%) together with unidentified products (*c.* 12%)

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*p = polarized.

(GLC) was distilled from the reaction mixture at 30 °C/1 mmHg. Preparative GLC of the mixture afforded 4.6 g of the pure dimer **4** (b.p., 99–100 °C). Mass spectrum: 324 (1.2) $[M]^+$; 255 (24) $[M-CF_3]^+$; 236 (9) $[M-CF_4]^+$; 224 (4) $[M-C_2F_4]^+$; 205 (11) $[M-C_2F_5]^+$; 186 (8) $[M-2CF_3]^+$; 162 (100) $[M-C_4F_6]^+$; 155 (14) $[M-C_2F_4-CF_3]^+$; 93 (32) $[M-C_4F_6-CF_3]^+$; 69 (21) $[CF_3]^+$. IR (cm^{-1}): 1785 (vs). Raman (cm^{-1}): 1784 (vs, p). ^{19}F NMR $-\delta$: 14.7 (dddd, F(1)); 31.1 (ddddddd, F(2)); 112.39 (ddm, F(3)); 91.94 (m, F(4)); 48.16 and 50.06 (F(5) and F(6), AB-system with additional coupling) ppm. Coupling constants: *J*(1–2), 51; *J*(1–3), 38; *J*(1–4), 7; *J*(1–?), 5; *J*(2–3), 119; *J*(2–4), 17; *J*(2 – ?), 13.5; *J*(2–?), 6; *J*(5–6), 217 Hz. ^{13}C NMR δ: 93.24 (d, C(1), C(2)); 113.94 (ddd, C(3), C(4)); 120.46 (ddt, C(5), C(7)); 156.8 (ddd, C(6), C(8)) ppm. Coupling constants: *J*(C–F): *J*(1–6), 285; *J*(6–2), 290; *J*(6–3), 40; *J*(5–1,2), 20; *J*(5–3), 237.5; *J*(5–4), 52.5; *J*(4–5), 285; *J*(4–6), 305; *J*(4–4), 25; *J*(1–4), 225 Hz. Analysis: Found: C, 29.80; F, 70.08%. C_8F_{12} requires C, 29.63; F, 70.37%.

*Dodecafluorotricyclo[4.2.0.0.^{2,5}]octane (**5**)*

Bromine (8 g) was added gradually to 21.6 g of a water-cooled mixture of dimers **3** (27.5%), **5** (7%), **4** (65.6%) and dimer **1** (traces) (^{19}F NMR spectroscopy). After 30 min, the mixture was sealed in a glass ampoule and left exposed to light at 20 °C. After 24 h, the mixture obtained was distilled affording: (a) a mixture of dimers **1** (*c.* 15%), **5** (*c.* 40%), **2** (*c.* 5%) and bromination products (*c.* 40%) (GLC) (b.p., 80–120 °C, 2.6 g); and (b) a mixture of bromides (b.p., 160–250 °C, 15 g). The residue left amounted to 2.5 g. Pure dimer **5** (b.p., 92 °C) was isolated from fraction (a) by preparative GLC methods. Mass spectrum: 324 (1) $[M]^+$; 305 (8) $[M-F]^+$; 255 (38) $[M-CF_3]^+$; 236 (12) $[M-CF_4]^+$; 224 (16) $[M-C_2F_4]^+$; 205 (44) $[M-C_2F_5]^+$; 186 (15) $[M-2CF_3]^+$; 162 (100) $[M-C_4F_6]^+$; 155 (23) $[M-C_2F_4-CF_3]^+$; 117 (9) $[M-3CF_3]^+$; 100 (12) $[C_2F_4]^+$; 93 (55) $[M-C_4F_6-CF_3]^+$; 69 (44) $[CF_3]^+$. IR: no absorption over the range 1600–1900 cm^{-1}. Raman (cm^{-1}): 1733 (vw). ^{19}F NMR $-\delta$: 41.62 and 49.40 (F(1) and F(2), AB-system with additional coupling); 112.45 (m, F(3); *J*(1–2), 230 Hz) ppm. Analysis: Found: C, 29.98; F, 70.01%. C_8F_{12} requires: C, 29.63; F, 70.37%.

*X-Ray analysis of **5***

A single crystal of dimer **5** was grown from the liquid in the sealed capillary into a thin-walled capillary (diameter, *c.* 0.4 mm) by the 'zone melting' method [32] at −30 °C to −35 °C directly on a Syntex $P2_1$ diffractometer equipped with an LT-1 low-temperature device. The single crystal obtained was slowly cooled to −55 °C and the first set of diffraction data (λ Mo, $\theta/2\theta$ scanning, $2\theta \leqslant 65°$, 1473 reflections, 1326 of them with $I \geqslant 2\sigma$) collected at this temperature. The second set of diffraction data (measured with great accuracy) was obtained from the same crystal at −120 °C ($2\theta \leqslant 93°$, 3235 reflections, 2996 of them with $I \geqslant 2\sigma$). The structure was solved by direct methods using the MULTAN program and refined by a leastsquares technique using the block–diagonal anisotropic approximation. Crystals of dimer **5** were triclinic at -55 °C and -120 °C: $a = 5.680(1)$ and $5.634(1)$; $b = 6.278(2)$ and $6.237(2)$; $c = 6.932(2)$ and $6.890(2)$ Å; $\alpha = 75.36(2)$ and $75.52(2)$; $\beta = 78.07(2)$ and $78.37(2)$; $\gamma = 79.81(2)$ and $80.63(2)$°; $V = 232.0(1)$ and $228.0(1)$ Å^3; $Z = 1$; space group P$\bar{1}$; centrosymmetric molecule.

Refinement of data obtained at -55 °C was completed at $R = 0.062$ and $R_w = 0.079$ using 1220 reflections with $|F| \geqslant 12\sigma(F)$. The diffraction data obtained at -120 °C were refined to $R = 0.054$ and $R_w = 0.060$ using 2748 independent reflections with $|F| \geqslant 8\sigma(F)$. The errors in determining the positional and thermal parameters of the structure at -120 °C were approximately one half of those in the previous refinement.

To obtain the most accurate values of the positional, and particularly the thermal, parameters for the atoms in molecule **5**, not subjected to shift due to chemical bond formation, high-angle refinement of low-temperature (-120 °C) data using 1672 reflections with $|F| \geqslant 8\sigma(F)$ and $\sin\theta/\lambda \geqslant 0.65$ Å^{-1} was carried out. This refinement was converged to $R = 0.036$, $R_w = 0.037$ and $GOF = 1.87$. The results of the refinement are listed in Table 1. It should be noted that the errors in determining the structural parameters for the high-angle refinement were 3–4-times lower than for data collected at -55 °C.

The molecular structure of **5** and its geometrical parameters (high-angle refinement at -120 °C) are shown in Fig. 1. An analysis of the anisotropic thermal parameters for molecule **5** resulted in poor agreement between the calculated and experimental data if all the atoms in the molecule were included in the calculation (R_u was equal to 14.7% at -55 °C and 12.5% at -120 °C). This agreement was improved appreciably if only the carbon atoms of the tricyclic framework were involved ($R_u = 3.6$ and 1.6%, respectively), i.e. only the carbon skeleton of the molecule may be regarded as rigid. Librational corrections to the bond lengths were 0.004–0.006 Å at -55 °C and

TABLE 1

Atomic coordinates for the structure of dimer **5** ($\times 10^4$) and their equivalent isotropic thermal parameters B_{eq} (Å^2) as obtained from high-angle refinement data

Atom	x	y	z	B_{eq}
F(1)	−2677(1)	2051(1)	2004(1)	1.78(1)
F(2)	2913(1)	540(1)	1669(1)	1.83(1)
F(3)	1527(2)	−3038(2)	4249(1)	2.54(1)
F(4)	1580(1)	−4585(1)	1734(1)	2.41(1)
F(5)	−3107(2)	−1833(1)	4481(1)	2.40(1)
F(6)	−3242(1)	−3282(1)	1947(1)	2.25(1)
C(1)	−1538(1)	320(1)	1218(1)	1.22(1)
C(2)	1351(1)	−471(1)	1049(1)	1.25(1)
C(3)	781(1)	−2766(1)	2467(1)	1.56(1)
C(4)	−2021(1)	−2012(1)	2614(1)	1.46(1)

0.002–0.003 Å at -120 °C. The parameters of the translational and librational tensors were virtually isotropic.

The X-ray data obtained were used as a zero approximation in the free-state geometry calculations of molecule **5** by the molecular mechanics method. In order to establish the qualitative peculiarities of the electron distribution in molecule **5**, the deformation electron density (DED) maps in the plane of the cyclobutane fragments [Fig. 2(a, b)] were constructed, as well as the section perpendicular to the plane of the central cycle and passing through the C(1) and C(2) atoms (Fig. 3). For the calculation of these sections, 1042 small-angle reflections with $\sin \theta/\lambda \leqslant 0.65$ Å^{-1} were used.

cis,trans-*Dodecafluoro-1,5-cyclo-octadiene (**6**)*

A mixture (12 g) containing 29% of dimer **3** and 71% of dimer **4** was heated in a sealed glass ampoule at 150 °C for 35 h. The mixture of dimers obtained had the following composition: 16% of **3**, 71% of **4**, 2% of **1**, *c.* 1.5% of **5**, *c.* 7.5% of **6** and 2% of a polymer (^{19}F NMR spectroscopy). The conversion of dimer **3** was 44%. Yields of dimers (%): **1**, 17; **5**, 10; **6**, 57; and polymer, 16. Using preparative GLC methods, 0.6 g of dimer **6**, containing *c.* 15% of dimer **4**, was isolated from the mixture obtained. Dimer **6** was stored in liquid nitrogen. Mass spectrum: 324 (0.8) $[M]^+$; 255 (19) $[M-CF_3]^+$; 236 (7) $[M-CF_4]^+$; 205 (12) $[M-C_2F_5]^+$; 186 (8) $[M-2CF_3]^+$; 162 (100) $[M-C_4F_6]^+$; 155 (6) $[M-CF_3-C_2F_4]^+$; 93 (54) $[M-C_4F_6-CF_3]^+$; 69 (24) $[CF_3]^+$. IR (cm^{-1}): 1668 (m). Raman (cm^{-1}): 1681 (s, p); 1670 (s, p). ^{19}F NMR $-\delta$: 40.58; 42.0; 44.0; 45.46; 48.0; 51.7; 61.6 (intensity ratio: 3.4:2.3:1:4.3:1:5.1:4.1) ppm. ^{13}C NMR δ: 145.0 (dm, C(1), C(2), C(5), C(6)); 110.0 (tm, C(3), C(4), C(7), C(8)) ppm. Coupling constants: J(1–F), 174.5; J(3–F$_2$), 274 Hz.

Complex (2:1) of cis,trans-*dodecafluoro-1,5-cyclo-octadiene with rhodium dicarbonyl acetylacetonate (**12**)*

A mixture of dimers **6** (85%) and **4** (15%) (0.1 g) was added to a solution of 0.025 g of rhodium dicarbonyl acetylacetonate in 5 ml of a 1:1 ether/hexane mixture. The homogeneous mixture was allowed to evaporate at 20 °C. After 15 h, the liquid above the crystals of complex **12**, which contained only dimer **6** (^{19}F NMR spectroscopy), was removed by means of a pipette.

*X-Ray analysis of **6***

Crystals of complex **12** are monoclinic, at -120 °C: $a=8.636(3)$; $b=34.315(9)$; $c=8.700(2)$ Å; $\beta=91.93(3)$°; $V=2567.9(9)$ Å^3; $Z=4$, space group $P2_1/n$. A total of 3127 independent reflections were collected, 2672 of them with $|F|\geqslant 8\sigma$ being used for further calculation and refinement. The structure was solved by heavy-atom techniques and refined using the anisotropic block–diagonal approximation. Hydrogen atoms were located from a difference synthesis of the electron density and their positions were established with $B_{iso}=3.0$ Å^2. Structure **12** was refined to $R=0.040$ and $R_w=0.045$. The atomic coordinates are listed in Table 2. A general view of

TABLE 2

Atomic coordinates ($\times 10^4$; for Rh, $\times 10^5$) in complex **12** (F and H atoms list the numbers of the C atoms connected to them)

Atom	x	y	z
Rh	25724(6)	14685(1)	−795(5)
O(1)	4863(6)	1923(1)	1827(5)
O(2)	922(5)	1121(1)	−1195(4)
O(3)	728(5)	1596(1)	1524(4)
F(1)	3143(4)	1289(1)	−3177(4)
F(2)	3328(4)	2226(1)	−1350(4)
F(3,1)	593(4)	2302(1)	−2496(4)
F(3,2)	383(4)	1705(1)	−3322(4)
F(4,1)	2368(4)	1791(1)	−5403(4)
F(4,2)	1047(5)	2329(1)	−5401(4)
F(5)	3312(5)	2731(1)	−4388(5)
F(6)	6081(5)	2508(1)	−3863(4)
F(7,1)	7248(4)	1860(1)	−3995(4)
F(7,2)	5240(4)	1585(1)	−5091(4)
F(8,1)	6109(4)	1271(1)	−2385(4)
F(8,2)	6041(4)	1836(1)	−1246(4)
F(15)	1574(4)	391(1)	945(4)
F(16)	3463(4)	1140(1)	2951(4)
F(17,1)	5607(4)	1011(1)	951(4)
F(17,2)	4156(4)	630(1)	−505(4)
F(18,1)	6518(4)	328(1)	1382(4)
F(18,2)	4222(4)	86(1)	1604(4)
F(19)	6598(4)	629(1)	4034(4)
F(20)	4482(5)	570(1)	6071(4)
F(21,1)	2382(5)	−27(1)	3736(4)
F(21,2)	1889(5)	287(1)	5832(4)
F(22,1)	−52(4)	397(1)	3529(4)
F(22,2)	1095(4)	917(1)	4394(4)
C(1)	3694(7)	1557(2)	−2095(7)
C(2)	2613(7)	1879(2)	−1832(7)
C(3)	1402(8)	1997(2)	−3029(7)
C(4)	2124(8)	2120(2)	−4599(7)
C(5)	3581(8)	2345(2)	−4406(7)
C(6)	5015(8)	2231(2)	−4131(7)
C(7)	5707(7)	1830(2)	−3927(7)
C(8)	5353(7)	1618(2)	−2368(7)
C(9)	4023(7)	1750(2)	1055(7)
C(10)	−30(7)	934(2)	−494(7)
C(11)	−26(7)	935(2)	1261(7)
C(12)	−183(7)	1346(2)	1885(7)
C(13)	−1183(8)	686(2)	−1335(8)
C(14)	−1480(8)	1436(2)	2897(8)
C(15)	1536(7)	731(2)	1809(7)
C(16)	3005(7)	975(2)	1498(6)
C(17)	4390(8)	753(2)	972(7)
C(18)	5088(7)	397(2)	1887(7)
C(19)	5208(7)	482(2)	3613(7)

(*continued*)

TABLE 2 (*continued*)

Atom	x	y	z
C(20)	4144(8)	457(2)	4615(7)
C(21)	2472(8)	325(2)	4407(7)
C(22)	1295(7)	596(2)	3524(7)
H(11)	−104	79	166
H(10,1)	−229	72	−105
H(10,2)	−106	72	−234
H(10,3)	−105	40	−102
H(14,1)	−163	126	359
H(14,2)	−139	167	328
H(14,3)	−251	144	231

complex **12** with numbering of the atoms and the important geometric parameters included is shown in Fig. 4.

The thermal reaction of cis-*1,2-bis(trifluorovinyl)-1,2,3,3,4,4,-hexafluorocyclobutane (3) [Reaction (4), Scheme 1]*

A mixture (1 g) containing 59% of dimer **3** and 41% of dimer **4** was heated in a sealed glass ampoule. The reaction conditions, product composition and yields are listed in Table 3.

The thermal reaction of trans-*1,2-bis(trifluorovinyl)-1,2,3,3,4,4-hexafluorocyclobutane (4) [Reaction (3), Scheme 1]*

Dimer **4** (1 g) was heated in a sealed glass ampoule. The reaction conditions, product composition and yields are listed in Table 4.

The thermal reaction of dodecafluorotricyclo[4.2.0.0^{2,5}]octane (5) [Reaction (5), Scheme 1]

A mixture (1 g) containing 96.5% of dimer **5** and 3.5% of dimer **4** was heated in a sealed glass ampoule at 150 °C. The reaction time, product composition and yields are listed in Table 5.

The thermal reaction of cis,trans-*dodecafluoro-1,5-cyclo-octadiene (6) [Reaction (6), Scheme 1]. Poly(*cis,trans-*dodecafluoro-1,5-cyclo-octadiene)*

Method a

A mixture containing 81.5% of dimer **6** and 18.5% of dimer **4** was left at − 190 °C. After 35 d, a mixture of the following composition was obtained: 18.5% of dimer **4**, 58% of dimer **6** and 23% of a polymer (^{19}F NMR spectroscopy). Conversion of dimer **6** was 29%, polymer yield was 100%. The ^{19}F NMR spectrum of dimer **6** in carbon tetrachloride (*c.* 20% solution) could be observed after two months (20 °C).

Method b

Dimer **6** (0.2 g) was left at 20 °C in a sealed ampoule. After 15 h, a solid polymer and traces of dimers **6** and **4** (^{19}F NMR spectroscopy) were detected.

TABLE 3

Thermal reaction of *cis-F*-divinylcyclobutane (**3**). Reaction conditions, product composition and yields

Temperature (°C)	Time (h)	Product mixture composition (%)[a]						Conversion of **3** (%)	Yield (%)[a]			
		4	**3**	**5**	**1**	**6**	polymer		**5**	**1**	**6**	polymer
150	18	41	39.4	5.3	1.5	10.0	2.8	33	27	7.6	51	14.3
	32	41	22.7	9.2	3.8	11.9	11.4	62	25.3	10.4	32.7	31.3
165	15	41	15.2	12.5	8.0	12.8	10.4	74.4	28.6	18.3	29.2	23.8
	35	41	2.5	6.7	23.0	6.3	20.5	96	11.8	40.7	11.1	36.3
185[b]	15	41	0	0	24.8	0	34.2	100	0	42	0	58

[a] According to ^{19}F NMR data.

[b] In addition to dimers **1**, **4** and a polymer, traces of dimer **2** were also found in the reaction mixture.

TABLE 4

Thermal reaction of *trans*-*F*-divinylcyclobutane (**4**). Reaction conditions, product composition and yields

Temperature (°C)	Time (h)	Product mixture composition (%)[a]			Conversion of **4** (%)	Yield (%)	
		4	**1**	**2**		**1**	**2**
165	35	94.5	4.2	1.3	5.5	76.4	23
185	15	83	15.1	1.9	17	88.8	11
200	20	47.8	48.3	3.9	53	92.5	7
	50[b]	2.7	89.1	8.2	97.3	91.6	8

[a] According to ^{19}F NMR data.

[b] In addition to dimers **1** and **2**, 0.5% of an unknown substance was also found; ^{19}F NMR $-\delta$: 35.08 (m); and 58.93 (m) ppm; intensity ratio, *c.* 2:1.

TABLE 5

Thermal reaction of *F*-tricyclo[4.2.0.0^{2,5}]octane (**5**). Product composition and yields

Time (h)	Product mixture composition (%)[a]					Conversion of **5** (%)	Yield (%)[a]		
	4	**5**	**1**	**6**	polymer		**1**	**6**	polymer
35	3.5	66.4	7.0	12.7	13.9	31	20.8	38	41.2
55	3.5	32.0	7.0	8.3	49.2	67	10.8	12.8	76.4
80	3.5	24.6	13.4	5.8	52.7	74.5	18.6	8.0	73.4
110	3.5	10.5	12.4	3.0	70.6	90	14.4	3.5	82.1

[a] According to ^{19}F NMR data.

Method c

Dimer **6** (1 g) containing *c.* 15% of dimer **4** was heated in a sealed glass ampoule at 150 °C for 42 h. A colourless polymer containing no dimer **1** (^{19}F NMR spectroscopy) was obtained. The polymer was washed with ether and dried. Yield, 0.8 g (*c.* 90%). Decomposed > 460 °C. IR: no absorption over the range 1600–1900 cm^{-1}. Analysis: Found: C, 29.56; F, 70.50%. $(C_8F_{12})_n$ requires: C, 29.63; F, 70.37%.

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